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(54) Resin-containing organosiloxane compositions curable to silicone elastomers

(57) Organosiloxane compositions curable to silicone elastomers having improved weep properties are described. The compositions include an alkenyl-containing polydiorganosiloxane, an organohydrogensiloxane, a platinum-group metal catalyst and a MQ-type resinous organosiloxane copolymer; and a silicone elastomer prepared from such composition. A method of minimizing the leakage of a hydrocarbon fluid from a container using the silicone elastomer is also described.

Description

The present invention relates to organosiloxane compositions which yield, upon cure, silicone elastomers which exhibit improved weep properties. This invention also relates to silicone elastomers prepared from such organosiloxane compositions. The invention also relates to a method of minimizing the leakage of a hydrocarbon fluid from a container by sealing the container with a silicone elastomer of the present invention.

As used herein, the term "resin" describes a silicone composition wherein the molecular structure is arranged in a predominantly three dimensional network. The silicone resins utilized in the present invention are frequently designated "MQ" resins. MQ resins are macromolecular polymers comprised primarily of $R_3SiO_{1/2}$ and $SiO_{4/2}$ units (the M and Q units, respectively) wherein R is a functional or nonfunctional, substituted or unsubstituted organic group. Such resins may also include a limited number of $R_2SiO_{2/2}$ and $RSiO_{3/2}$ units, respectively referred to as D and T units. As used herein, the term "MQ resin" means that, on average, no more than 20 mole percent of the resin molecules are comprised of D and T units. Such resins are frequently produced by the method disclosed in US Patent No. 2,676,182.

When a silicone elastomer is placed in contact with or immersed in a hydrocarbon fluid, such as automobile engine oil, the silicone elastomer will absorb some or all of the hydrocarbon fluid. As a result, the silicone elastomer will swell. The greater the volume of fluid absorbed by the silicone elastomer the greater the swell of the elastomer. The amount of fluid absorbed by the elastomers is dependent upon the specific elastomer, the specific hydrocarbon fluid, the length of time of exposure and the temperature.

When a silicone elastomer which has been immersed in a hydrocarbon fluid at ambient temperature is subsequently heated, the silicone elastomer will absorb more of the hydrocarbon fluid. When this silicone elastomer is then allowed to cool to ambient temperatures, some of the absorbed hydrocarbon fluid will bleed out of the silicone elastomer. The weep properties of an elastomer is a measure of the tendency of the hydrocarbon fluid to bleed from the elastomer. The weep number of an elastomer is the difference between that elastomer's weight uptake of a hydrocarbon fluid at elevated and room temperatures, based on 100 grams of elastomer.

Organosiloxane compositions curable to silicone elastomers based upon vinyl-containing polydiorganosiloxane polymers, organohydrogensiloxanes containing silicon-bonded hydrogen atoms and platinum group containing catalysts are well known in the art. The silicone elastomers which such compositions yield upon cure are well known for their high swell and high weep properties.

The prior art is represented by U.S. Patent No. 3,249,581; U.S. Patent No. 4,322,518; U.S. Patent No. 4,830,925; U.S. Patent No. 4,871,782; European Patent Publication No. 0 509 515 A1; U.S. Patent No. 5,164,461; U.S. Patent No. 5,292,586; Japanese Kokai Patent Publication No. 07-216307 and U.S. Patent No. 5,574,073.

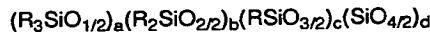
The present inventors discovered that MQ resins can be added to organosiloxane compositions adapted for gasket use to produce new compositions which have reduced weep properties. The compositions of the present invention, unlike the compositions described above, contain low levels of MQ resins and yield, upon cure, silicone elastomers having improved swell and weep properties.

One of the methods of sealing valve covers, rocker covers and oil pans in automotive engines is through the use of cured-in-place gaskets. These gaskets are produced by extruding a bead of sealant material onto the part to be used and curing the material in place. Since the gasket will be exposed to oils and other hydrocarbon fluids and will be repeatedly heat-cycled as the engine is turned on and off, the weep properties of the material must be minimized.

The organosiloxane composition of the present invention comprises an alkenyl-containing polydiorganosiloxane, an organohydrogensiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule, a platinum group catalyst and a resinous organosiloxane copolymers.

This invention relates to an organosiloxane composition curable to a silicone elastomer comprising:

- 45 (A) an alkenyl-containing polydiorganosiloxane having an average of at least two silicon-bonded alkenyl groups per molecule;
- (B) an organohydrogensiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule, the amount of organohydrogensiloxane present being sufficient to provide a ratio of silicon-bonded hydrogen atoms in component (B) to silicon-bonded alkenyl groups in component (A) of 0.8:1 to 3:1;
- 50 (C) a platinum group catalyst sufficient for curing the organosiloxane composition; and
- (D) a resinous organosiloxane copolymer having, an average of at least two alkenyl groups per molecule, a number average molecular weight (M_n) between 400 and 15,000 g/mole having the empirical formula:



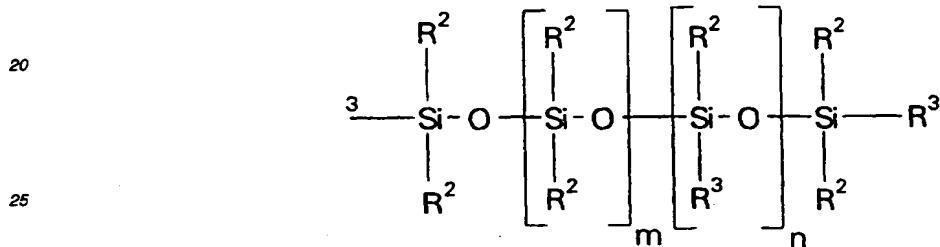
55 wherein $a > 0$, $d > 0$, $b \geq 0$, $c \geq 0$, $a + b + c + d = 1$, $0 \leq (b + c) \leq 0.2$ and R is a monovalent radical independently selected from hydrogen, hydroxyl, alkyl, alkenyl, alkoxy, -OZ and Z groups; wherein Z is a fluorine atom-containing group; and wherein the sum of the average number of

silicon-bonded alkenyl groups per molecule in component (A) and the average number of silicon-bonded hydrogen atoms per molecule in component (B) is greater than four.

Preferably the organosiloxane composition of the present invention comprises 100 parts by weight of component (A), 5 to 100 parts by weight of component (B), per 100 parts by weight of component (A), component (C) in an amount sufficient to cure the organosiloxane composition and 1 to 10 parts by weight of component (D) per 100 parts by weight of component (A).

Component (A) is an alkenyl-containing polydiorganosiloxane. It is the major component of the composition of the present invention. In order for the polymer to properly crosslink, an average of at least two alkenyl groups per molecule are needed. Component (A) contains alkenyl groups having from 2 to 12 carbon atoms. Alkenyl groups are represented by the formula $-R^1CH=CH_2$, where R^1 represents an alkylene group or a single bond. The alkylene group can be linear or branched. Preferred alkenyl groups include vinyl, 2-propenyl, 3-butenyl, 5-hexenyl, 7-octenyl and 10-undecenyl. More preferred alkenyl groups are vinyl and hexenyl. In preferred embodiments, at least one alkenyl group is located at the terminal of the molecule chain. In more preferred embodiments, at least two alkenyl groups are located at two of the terminals of the molecular chain.

In preferred embodiments, component (A) is represented by the general formula:



wherein each R^2 is individually selected from unsubstituted and substituted monovalent hydrocarbon groups containing from 1 to 20 carbon atoms; R^3 is R^2 or an alkenyl group and $m \geq 0$; and the value of n is selected such that component (A) has an average of at least two alkenyl groups per molecule. Preferably, R^2 is an unsubstituted monovalent hydrocarbon group having less than 7 carbon atoms or a halogenated alkyl group having less than 7 carbon atoms. More preferably, R^2 is alkyl group, such as methyl or ethyl, a cycloalkyl group such as cyclohexyl, aryl group, such as phenyl, or a substituted alkyl group, such as chloromethyl, 3-chloropropyl or 3,3,3-trifluoropropyl. Most preferably, R^2 is methyl.

35 In preferred embodiments, n is zero.

Generally, the siloxane is polymerized to a viscosity of from 0.1 to 500 Pa · s at 25°C., preferably from 1 to 100 Pa · s. It is possible to use either higher or lower viscosity polymers.

The alkenyl-containing polydiorganosiloxane of the present invention may be a homopolymer, or a copolymer. A single alkenyl-containing polydiorganosiloxane can be used or a mixture of different alkenyl-containing polydiorganosiloxanes can be used.

40 Component (B) of the present invention is an organohydrogensiloxane containing an average of at least two silicon-bonded hydrogen atoms per molecule. It is used to crosslink the composition of the present invention. The silicone-bonded hydrogen atoms in component (B) react with the alkenyl groups in component (A) in order to cure the composition of the present invention. In order for the composition of the present invention to cure to a silicone elastomer, the sum of the average number of silicon-bonded alkenyl groups per molecule in component (A) and the average number of silicon-bonded hydrogen atoms in component (B) must be greater than 4.

45 Organohydrogensiloxanes that may be used as component (B) preferably contain an average of more than two silicon-bonded hydrogen atoms per molecule and more preferably contain an average of at least three silicon-bonded hydrogen atoms per molecule. The remaining valances on the silicon atoms are satisfied with organic groups selected from alkyl groups having less than 7 carbon atoms, halogenated alkyl groups having less than 7 carbon atoms and phenyl groups. Preferred alkyl groups are methyl, ethyl and hexyl. Most preferred alkyl groups are methyl groups. Preferred halogenated alkyl groups are perfluorobutylethyl and 3,3,3-trifluoropropyl groups.

The organohydrogensiloxane of component (B) can have a linear or branched structure and can be a homopolymer, a copolymer or a mixture of these types of polymers.

50 A preferred linear organohydrogensiloxane has a viscosity of from 0.01 to 10 Pa · s at 25°C. and comprises dialkylsiloxane and alkylhydrogensiloxane units with trialkylsiloxy terminal units. The alkyl groups contain from 1 to 4 carbon atoms and are most preferably methyl. In preferred embodiments, component (B) comprises two types of organohydrogensiloxanes, one of which is a polymethylhydrogensiloxane and the other of which is a copolymer containing methyl-

hydrogensiloxane and dimethylsiloxane units. Component (B) is present in an amount ranging from 0.5 to 100 parts by weight per 100 parts of component (A). In preferred embodiments, component (B) is present in an amount ranging from 1 to 25 parts per 100 parts of component (A). In more preferred embodiments, component (B) is present in an amount ranging from 1 to 10 parts per 100 parts of component (A).

The molar ratio of silicon-bonded hydrogen atoms to vinyl or other ethylenically unsaturated hydrocarbon groups in compositions curable by a hydrosilation reaction is important with respect to the properties of the cured elastomer. The optimum ratio for the present curable compositions will be determined at least in part by the molecular weight of the alkenyl-containing polydiorgano-siloxane and the type of curing agent. An effective molar ratio of silicon-bonded hydrogen atoms to silicon-bonded alkenyl groups is in the range of 0.8:1 to 3:1, with a preferred range of 1.2:1 to 1.69:1.

Component (C) is a metal from the platinum group of the periodic table or a compound of such a metal. These metals include platinum, palladium and rhodium. Platinum and platinum compounds are preferred based on the high activity level of these catalysts in hydrosilylation reactions. Catalysts that may be used as component (C) in the organosiloxane composition of the present invention are any of the known forms that are effective in promoting the reaction of -SiH groups with silicon-bonded alkenyl groups. Suitable forms of platinum include chloroplatinic acid, platinum compounds and complexes of platinum compounds with unsaturated organic compounds or with siloxanes having silicon-bonded groups containing ethylenically unsaturated groups. Additional examples of suitable platinum catalysts include complexes of platinous halides or chloroplatinic acid with divinyldisiloxane and tetramethyldisiloxane. Suitable platinum catalysts are described in U.S. Patent No. 3,419,593.

The concentration of component (C) in the present composition is equivalent to a platinum concentration of from

20 The concentration of component (C) in the product is 0.1 to 500 parts by weight of platinum metal, preferably from 5 to 100 parts by weight of platinum metal, per million parts (ppm), based on the combined weights of components A and B.

Component (D) is a resinous organosiloxane copolymer having an average of at least two alkenyl groups per molecule, a number average molecular weight (M_n) between 400 and 15,000 and having the empirical formula:

25 $(R_3SiO_{1/2})_a(R_2SiO_{2/2})_b(RSiO_{3/2})_c(SiO_{4/2})_d$

wherein $a > 0$, $d > 0$, $b \geq 0$, $c \geq 0$, $a + b + c + d = 1$, $0 \leq (b + c) \leq 0.2$ and R is a monovalent radical independently selected from hydrogen, hydroxyl, alkyl, alkenyl, alkoxy,

-OZ and Z groups; wherein Z is a fluorine atom-containing group.

30 According to a preferred embodiment the present invention refers to a resinous organosiloxane copolymer having at least one fluorine atom-containing group per molecule, an average of at least two alkenyl groups per molecule, a number average molecular weight (Mn) between 400 and 15,000 g/mole and having the empirical formula:

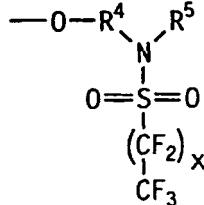
$$(R_3SiO_{1/2})_a(R_2SiO_{2/2})_b(RSiO_{3/2})_c(SiO_{4/2})_d$$

wherein $a > 0$, $d > 0$, $b \geq 0$, $c \geq 0$, $a + b + c + d = 1$, $0 \leq (b + c) \leq 0.2$, and R is a monovalent radical independently selected from hydrogen, hydroxyl, alkyl, alkenyl, alkoxy,

-OZ and Z; wherein Z is a fluorine atom-containing group.

In preferred embodiments, the fluorine-containing group Z is bonded to a silicon atom on a M unit via an oxygen atom.

40 Preferred alkyl groups are methyl and ethyl. The preferred alkenyl group is vinyl. The preferred alkoxy groups are methoxy and ethoxy. The -OZ group is selected from the general formula:



55 and general formula:



wherein R^4 is an alkylene group having 2 to 6 carbon atoms and $0 \leq x \leq 12$ and R^5 is an alkyl group having 1 to 6 carbon atoms. In preferred embodiments, the value of x is from 3 to 11. More preferably, the value of x is from 3 to 7.

The resinous organosiloxane of component (D) must contain an average of at least two alkenyl groups per molecule. In preferred embodiments, component (D) contains an average of 2 to 6 vinyl groups per molecule. In more preferred embodiments, component (D) has 4 to 6 vinyl groups per molecule.

In preferred embodiment of the present invention, component (D) is present in an amount ranging from 0.5 to 10 parts by weight per 100 parts of component (A). In more preferred embodiment, component (D) is present in an amount ranging from 0.5 to 5 parts by weight per 100 parts of the organosiloxane composition.

The resinous organosiloxane copolymer D has a number average molecular weight (M_n) between 400 and 15,000 g/mole and preferably between 400 and 7,500 g/mole and most preferably between 400 and 4000 g/mole. When M_n is greater than 15,000, the resins begin to lose their solubility in most solvents and tend to include significant amounts of gel.

Regardless of the other R groups present in component (D), it is preferred that at least sixty mole percent of the monovalent organic radicals associated with the resinous organosiloxane copolymer are methyl groups.

The ratio of M units to Q units is component (D) is from 0.8:1 to 4:1. In preferred embodiments, the ratio is from 1.6:1 to 4:1. In more preferred embodiments, the ratio is from 2:1 to 4:1.

MQ silicone resins are generally produced in such a manner that the resin macromolecules are dissolved in a solvent, which is typically, but not always, an aromatic solvent. Thus, as used herein, the term "solventless" means that substantially all the liquid solvent has been removed from the "solid" resin phase. It is known in the art to produce solventless forms of silicone resins.

The aforementioned values assigned to a, b, c and d define the "MQ" nature of the resins used to practice the present invention and distinguish them from silsesquioxane-type resins.

Mixtures of the aforementioned polydiorganosiloxane, crosslinking agent, platinum catalyst and MQ resin may begin to cure at ambient temperatures. To obtain a longer working time or "pot life", the activity of the catalyst under ambient conditions can be retarded or suppressed by addition of a suitable inhibitor. Known inhibitors include the acetylenic compounds disclosed in U.S. Patent No. 3,445,420. Acetylenic alcohols such as 2-methyl-3-butyn-2-ol and ethynyl cyclohexanol constitute a preferred class of inhibitors that will suppress the activity of a platinum-containing catalyst at 25 °C, but cure rapidly at temperatures of 70°C. or higher.

Examples of suitable inhibitors include ethylenically or aromatically unsaturated amides, acetylenic compounds including acetylenic alcohols and silylated acetylenic alcohols, ethylenically unsaturated isocyanates, olefinic siloxanes, unsaturated hydrocarbon diesters, conjugated ene-ynes, cyclic siloxanes, hydroperoxides, nitriles and diaziridines.

Preferred inhibitors include ethynylcyclohexanol and methylbutynol, diallyl maleate and dimethyl maleate, diethyl fumarate, diallyl fumarate and bis-(methoxyisopropyl) maleate, conjugated ene-ynes such as those disclosed in U.S. Patent Nos. 4,465,818, 4,472,563 and 4,559,396 and cyclic siloxanes such as methylvinyltetra-cyclosiloxane and methylvinylpentacyclosiloxane.

In order to obtain satisfactory levels of physical strength, compositions of polydiorganosiloxane are commonly reinforced with one or more fillers such as fumed silica. Any finely divided form of silica can be used as a reinforcing filler. Colloidal silicas are preferred because of their relatively high surface area, which is typically at least 50 square meters per gram. Fillers having surface areas of at least 250 square meters per gram are preferred for use in the present method. Colloidal silicas can be prepared by precipitation or a fume process. Both of these preferred types of silica are commercially available.

The amount of finely divided silica used in the present compositions is at least in part determined by the physical properties desired in the cured elastomer. Liquid or pumpable polyorganosiloxane compositions typically contain from 10 to 60 percent by weight of silica, based on the weight of polydiorganosiloxane. This value is preferably from 30 to 50 percent.

Typically, the reinforcing filler is modified with silica treating agents to prevent a phenomenon referred to as "creping" or "crepe hardening" during processing of the curable composition. Preferably, a portion of the silica treating agent contains at least one silicon-bonded alkenyl radical per molecule. These silica treating agents are typically liquid hydroxyl terminated polydiorganosiloxanes containing an average of from 2 to 20 repeating units and at least one alkenyl radical per molecule. They include organosilicon compounds such as hexaorganodisiloxanes and hexaorganodisilazanes that contain at least one alkenyl radical per molecule and hydrolyze under the conditions used to treat the silica to form compounds with silicon-bonded hydroxyl groups. Small amounts of water are often added to the composition during the filler treatment step to facilitate the process.

Preferably at least a portion of the silicon-bonded hydrocarbon radicals other than alkenyl that are present on the silica treating agent are identical to a majority of the hydrocarbon radicals present in the polydiorganosiloxane. The alkenyl radicals on the silica treating agent are preferably vinyl, particularly when alkenyl radicals containing at least four carbon atoms are present on the polydiorganosiloxane. It is believed that silica treating agents function by reacting with silicon-bonded hydroxyl groups present on the surface of the silica particles to reduce interaction between these parti-

cles and the polydiorganosiloxanes.

The filler can also be a non-reinforcing or extending filler of finely ground particles of oxides or hydroxides or carbonates of such as silicon, calcium, magnesium, barium, or zinc, with silicon oxide (quartz) and calcium carbonate as preferred non-reinforcing fillers.

5 To enhance the adhesion of the cured elastomer to a substrates, the organosiloxane composition of the present invention may also contain an adhesion promoter.

The compositions of this invention can be prepared by a simple mixing of the components and any optional ingredients. However, when reinforcing fillers are included, the fillers are often treated *in situ* by first combining the polydiorganosiloxane, filler, filler treating agents and enough water to facilitate the filler treating process and then heating the 10 mixture. For example, heating for 1 to 4 hours at 170°C. has been found to provide good filler treatment. The heating may also be conducted at reduced pressure to assist in removing any excess water and the ammonia formed in the process. After filler treatment is completed, the remaining components are simply mixed into the composition. The equipment needed for the mixing depends upon the viscosity of the polydiorganosiloxane used and the amount of filler.

15 When the components of the present invention and any optional ingredients are mixed together, the composition will begin to cure unless a cure inhibitor is present. If the composition is not to be used immediately after mixing, it should be prepared in at least two parts. If the organohydrogensiloxane is placed in one part and the platinum catalyst is placed in another part, the individual parts will be shelf stable. The amounts of polydiorganosiloxane, organohydrogensiloxane and filler that are placed in each part can be varied to obtain the desired result. A convenient system distributes the ingredients into two parts so that the polydiorganosiloxane and filler are divided equally between the two 20 parts. The organohydrogensiloxane is added to one part and the platinum catalyst is added to the other part. This results in a two-part system where the two part are mixed together in equal amounts and the consistency of the two parts is about the same so that they can be easily mixed at the time of use. Other proportions of the ingredients can of course be used, as well as more than two parts if desired.

25 For application, the two parts of the composition may be mixed together and extruded into place on a substrate as a bead to form a gasket. After the gasket is formed on the substrate, it may be allowed to cure at ambient temperatures or it may be heated to accelerate the cure. In an alternative application method, the two parts of the composition may be mixed together and then placed in a mold, cured and then demolded.

30 The present invention also relates to a silicone elastomer that is prepared by (I) combining components A, B, C and D as described above, and (II) allowing the organosiloxane composition to cure.

35 The organosiloxane composition may also include optional ingredients as described above. The organosiloxane composition may be allowed to cured at ambient conditions, at elevated temperatures and/or elevated pressures.

The present invention also relates to a method of minimizing the leakage of hydrocarbon fluid from a container by sealing the container with the organosiloxane composition or the silicone elastomer of the present invention. In one embodiment, the method comprises the steps of (I) preparing an organosiloxane composition comprising components 40 A, B, C and D as described above; and (II) sealing the container by

- (i) applying the organosiloxane composition to a surface on the container; and
- (ii) allowing the composition to cure.

45 In an alternative embodiment, the method comprises the steps of (I) preparing an organosiloxane composition comprising components A, B, C and D as described above; and (II) allowing the composition to cure to a silicone elastomer; and (III) sealing the container by securing the cured elastomer to a surface on the container.

The surface on the container can be a small opening that can be sealed by applying the composition of the present invention or by adhering the silicone elastomer that results when the composition of the present invention is cured. The 50 surface can also be a surface on the container that mates with a cover or a lid for the container. The surface can also be a cover or a lid for the container. The organosiloxane composition or the cured silicone elastomer be applied to the lid or cover before the lid or cover is placed on the container.

55 The following examples are included for illustrative purposes only and should not be construed as limiting the invention which is properly set forth in the appended claims. All parts and percentages in the examples are by weight and viscosities were measured at 25°C. The organosiloxane compositions of the examples and the comparative examples were prepared as follows: The composition of the Comparative Example 1 was prepared by preparing Part A and Part B. Part A was prepared by mixing a portion of the dimethylvinylsiloxy-terminated polydimethylsiloxane and the next listed 7 ingredients of Part A and heating the mixture using 1034 MPa of steam. The mixture was then stripped to remove water, ammonia and some cyclic siloxane components. The remaining dimethylvinyl-siloxy-terminated polydimethylsiloxane and the calcium hydroxide were then admixed. The mixture was then allowed to cool to below 100°C. and the remaining ingredients were admixed. Part B was prepared by mixing a portion of the dimethylvinylsiloxy-terminated polydimethylsiloxane and the next listed 7 ingredients of Part B and heating the mixture using 150 psi (1034 MPa) of steam under a 15 inch (38 mm) vacuum. The mixture was then stripped to remove the water, ammonia and some of

the cyclic siloxane components. The remaining dimethylvinylsiloxy-terminated polydimethyl-siloxane was then admixed. The mixture was then allowed to cool to below 100°C. and the remaining ingredients were admixed.

A silicone elastomer was prepared from each of the compositions of the Examples and Comparative Examples by admixing Part A and the corresponding part B and curing the compositions, at 150°C. for the time listed on Tables 1 or 2. Approximately 0.5 grams of the mixture of Parts A and B for each of the Examples and Comparative Examples were placed on a steel slide. The composition was cured by placing the steel slide containing the composition into an oven at 150°C. for the number of minutes listed in Table 1 and 2.

The swell and weep properties of the silicone elastomers were determined according to the following method. Before the organosiloxane composition was applied to the steel slide, the slide was weighed. The weight of the steel slide was recorded as W_1 . After the organosiloxane composition was applied to the steel slide and cured, the weight of the cured elastomer and steel slide, W_2 was determined. The slide and cured elastomer were immersed in a hydrocarbon fluid for the number of hour listed on Tables 1 and 2 under "Swell Time". The hydrocarbon fluid was Mobil® 5W30 SG oil. "MOBIL" is a registered trademark of Mobil Oil Corporation of Fairfax, Va. The steel slide containing the cured silicone elastomer was then removed from the hydrocarbon fluid and the excess fluid was wiped from the slide and the elastomer. The slide and elastomer were then weighed and the weight was recorded as W_3 . The slide and the elastomer were allowed to set at room temperature for the number of hours listed on Table 1 or 2 as "Weep Time". The excess hydrocarbon fluid which had bled from the silicone elastomer during the "Weep Time" was wiped off the steel slide and silicone elastomer. The steel slide and the elastomer were then weighed and the weight was recorded as W_4 . The % swell at elevated temperature was calculated as follows:

$$\text{% swell at elevated temperature} = ((W_3 - W_1) - (W_2 - W_1)) / (W_2 - W_1).$$

The % swell at ambient temperature was calculated as follows:

$$\text{% swell at ambient temperature} = ((W_4 - W_1) - (W_2 - W_1)) / (W_2 - W_1).$$

The weep number (Weep #) was calculated as follows:

Weep # = % swell at elevated temperature - % swell at ambient temperature. Percent swell and weep numbers are recorder in Tables 1 and 2.

30 COMPARATIVE EXAMPLE 1

Part A

35 49 parts by weight of a liquid dimethylvinylsiloxy-terminated polydimethylsiloxane having a viscosity of 55,000 mPa · s at 25°C.
 3.69 parts by weight of a dimethylhexenylsiloxy-terminated dimethylsiloxane:methylhexenylsiloxane copolymer having a viscosity of 420 mm²/s.
 0.13 parts by weight of tetramethyldivinyldi-silazane
 40 6.15 parts by weight of hexamethyldisilazane 0.52 parts by weight of a hydroxyl-terminated polydimethylsiloxane fluid having a viscosity of approximately 41 mm²/s at 25°C; with a hydroxyl content of approximately 3.1 wt%.
 10.5 parts by weight of quartz having a typical particle size of less than 5 microns.
 18.4 parts by weight of amorphous silica having an average surface area of 400 m²/g.
 3.1 parts by weight water
 45 0.35 parts chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.65 weight percent platinum.
 2.11 parts by weight calcium hydroxide
 0.018 parts by weight toluene
 3.34 parts by weight of a mixture containing 40% by weight of carbon black and 60% by weight of trimethylsiloxy-
 50 terminated dimethylsiloxane.
 0.001 parts by weight aluminum acetylacetone
 2.05 parts by weight of a 20 wt% copper phthacyanine and 25 wt% carbon black in dimethylvinylsiloxy-terminated dimethylsiloxane.

55 Part B

52.4 parts by weight of a liquid dimethylvinylsiloxy terminated polydimethylsiloxane having a viscosity of 55,000 mPa · s at 25°C.

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3.94 parts by weight a dimethylhexenylsiloxy-terminated dimethylsiloxane:methylhexenylsiloxane copolymer having a viscosity of 420 mm²/s at 25°C.

0.14 parts by weight of tetramethyldivinyldi-silazane

6.57 parts by weight of hexamethydisilazane

5 11.3 parts by weight of quartz having a typical particle size of less than 5 microns.

19.71 parts by weight of amorphous silica having an average surface area of 400 m²/g.

3.3 parts by weight of water

0.04 parts by weight of 1-ethynyl-1-cyclohexanol 99%

10 0.56 parts by weight of a hydroxyl-terminated polydimethylsiloxane fluid having a viscosity of approximately 41 mm²/s at 25°C.; with a hydroxyl content of approximately 3.1 wt%.

1.97 parts by weight of dimethylsiloxane-methylhydrogensiloxane copolymer with methyl silsesquioxane having a silicon-bonded hydrogen content of approximately 0.81 wt%.

0.3 parts by weight of gamma-glycidoxypropyl-trimethoxysilane

15 COMPARATIVE EXAMPLE 2

Part A

25.00 g of Part A of Comparative Example 1

20 Part B

25.00 g of Part B of Comparative Example 1

25 EXAMPLE 1

Part A

23.36 g of Part A of Comparative Example 1.

30 Part B

23.36 g of Part B of Comparative Example 1.

1.73 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673.

35 2.35 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

0.1 g of a chloroplatinic acid complex of divinyltetramethydisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.05 g of bis(methoxymethylethyl)maleate.

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EXAMPLE 2

Part A

45 22.47 g of Part A of Comparative Example 1.

Part B

22.47 g of Part B of Comparative Example 1.

50 3.24 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673.

1.75 g of dimethylsiloxane:methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

0.05 g of a chloroplatinic acid complex of divinyltetramethydisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

55 0.025 g of bis(methoxymethylethyl)maleate.

EXAMPLE 3

Part A

5 6.74 g of Part A of Comparative Example 1.

Part B

6.74 g of Part B of Comparative Example 1.

10 0.97 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673. 0.54 g of dimethylsiloxane-methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

0.026 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

15 0.02 g of bis(methoxymethylethyl)maleate.

EXAMPLE 4

Part A

20 6.74 g of Part A of Comparative Example 1.

Part B

25 6.74 g of Part B of Comparative Example 1.

0.97 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673. 0.54 g of dimethylsiloxane-methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

0.026 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

30 0.02 g of bis(methoxymethylethyl)maleate.

EXAMPLE 5

Part A

35 6.74 g of Part A of Comparative Example 1.

Part B

40 6.74 g of Part B of Comparative Example 1.

0.97 g of an ethoxylated MQ resin was prepared according to the method of U.S. Patent No. 5,391,673. 0.54 g of dimethylsiloxane-methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

0.026 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

45 0.02 g of bis(methoxymethylethyl)maleate.

EXAMPLE 6

Part A

50 6.35 g of Part A of Comparative Example 1.

Part B

6.35 g of Part B of Comparative Example 1.

0.98 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673.

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1.33 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

0.005 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxyl endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

5 0.004 g of bis(methoxymethylethyl)maleate.

EXAMPLE 7

Part A

10 22.5 g of Part A of Comparative Example 1.

Part B

15 22.5 g of Part B of Comparative Example 1.

4.02 g of an ethoxylated MQ prepared according to the method of U.S. Patent No. 5,391,673.

0.99 g of dimethylsiloxane-methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

20 0.05 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxyl endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.025 g of bis(methoxymethylethyl)maleate.

EXAMPLE 8

25 Part A

22.5 g of Part A of Comparative Example 1.

Part B

30 22.5 g of Part B of Comparative Example 1.

4.14 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673.

0.87 g of dimethylsiloxane:methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

35 0.05 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxyl endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.025 g of bis(methoxymethylethyl)maleate.

EXAMPLE 9

40 Part A

22.5 g of Part A of Comparative Example 1.

45 Part B

22.5 g of Part B of Comparative Example 1.

4.21 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673. 0.8 g of dimethylsiloxane:methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

50 0.05 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxyl endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.025 g of bis(methoxymethylethyl)maleate.

EXAMPLE 10

Part A

5 22.5 g of Part A of Comparative Example 1.

Part B

22.5 g of Part B of Comparative Example 1.

10 4.02 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673. 1.98 g of dimethylsiloxane:methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

0.05 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

15 0.025 g of bis(methoxymethylethyl)maleate.

EXAMPLE 11

Part A

20 22.5 g of Part A of Comparative Example 1.

Part B

25 22.5 g of Part B of Comparative Example 1.

4.02 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673. 2.97 g of dimethylsiloxane:methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

0.05 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

30 0.025 g of bis(methoxymethylethyl)maleate.

EXAMPLE 12

35 Part A

3.71 g of Part A of Comparative Example 1.

Part B

40 3.71 g of Part B of Comparative Example 1.

0.82 g of an ethoxylated MQ resin prepared according to the method of U.S. Patent No. 5,391,673. 0.44 g of dimethylsiloxane:methylhydrogensiloxane copolymer having a viscosity of approximately 30 mm²/s and having a silicon-bonded hydrogen content of approximately 1%.

45 0.001 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.0005 g of bis(methoxymethylethyl)maleate.

EXAMPLE 13

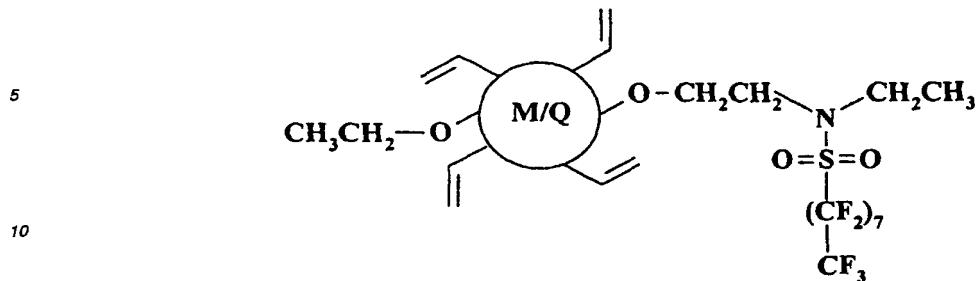
50 Part A

31.09 g of Part A of Comparative Example 1.

55 Part B

31.09 g of Part B of Comparative Example 1.

3.67 g of a fluorine atom-containing MQ having the general formula



15 (hereinafter "FMQ1"). FMQ1 was prepared as follows. An ethoxylated MQ resin, having a Mn of 1427, an average of approximately 4 vinyl groups per molecule, and an average of approximately 0.6 ethoxy groups per molecule was prepared according to the method of U.S. Patent No. 5,391,673. A flask was charged with 77.30 g of this ethoxylated M/Q resin and 50.06 g perfluoroalkylsulfonamido(N-ethyl)ethyl alcohol. The mixture was heated to 70°C. at which time 1.35 g tetrabutyltitanate (TBT) was added. The temperature was increased to 100°C. for 2 hours, then increased to 140°C. for 1 hour, and then was maintained at 120°C. for 1 hour before an additional 0.6 g of TBT was added. The reaction was allowed to proceed for an additional 4.5 hours before being stopped.

20 3.12 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane: methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

25 0.135 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.071 g of bis(methoxymethylethyl)maleate.

EXAMPLE 14

30 Part A

23.91 g of Part A of Comparative Example 1.

Part B

35 23.91 g of Part B of Comparative Example 1.

6.35 g of FMQ1.

5.4 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

40 0.233 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.124 g of bis(methoxymethylethyl)maleate.

EXAMPLE 15

45 Part A

18.08 g of Part A of Comparative Example 1.

50 Part B

18.08 g of Part B of Comparative Example 1.

8.24 g of FMQ1.

7.0 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

55 0.302 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.16 g of bis(methoxymethylethyl)maleate.

EXAMPLE 16

Part A

5 14.85 g of Part A of Comparative Example 1.

Part B

10 14.85 g of Part B of Comparative Example 1.

10.57 g of FMQ1.

8.98 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

0.387 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

15 0.205 g of bis(methoxymethylethyl)maleate.

EXAMPLE 17

Part A

20 12.47 g of Part A of Comparative Example 1.

Part B

25 12.47 g of Part B of Comparative Example 1.

13.23 g of FMQ1.

11.24 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

30 0.485 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.257 g of bis(methoxymethylethyl)maleate.

EXAMPLE 18

Part A

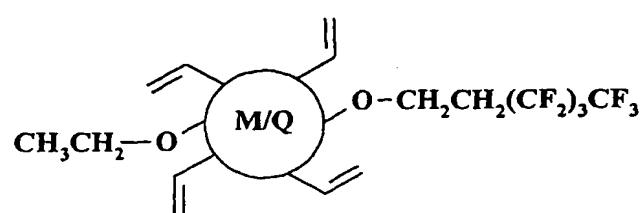
35 29.57 g of Part A of Comparative Example 1

Part B

40 29.57 g of Part B of Comparative Example 1.

2.88 g a fluorine atom-containing MQ resin having a Mn of approximately 5000, approximately 4 vinyl groups per molecule and having the general formula

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55 (hereinafter "FMQ2"). FMQ2 was prepared as follows. An ethoxylated MQ resin, having a Mn of 1427, an average of approximately 4 vinyl groups per molecule, and an average of approximately 0.6 ethoxy groups per molecule was prepared according to the method of U.S. Patent No. 5,391,673. A flask was charged with 20.00 g of this ethoxylated M/Q resin and 6.21 g perfluorobutylethanol. The mixture was heated to 120°C. at which time 0.262 g TBT was

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added. The reaction was allowed to proceed for an additional 12 hours.
1.28 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.
5 0.067 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.
0.039 g of bis(methoxymethylethyl)maleate.

EXAMPLE 19

10 Part A

21.91 g of Part A of Comparative Example 1.

Part B

15 21.91 g of Part B of Comparative Example 1.
2.39 g of FMQ2-type resin having a molecular weight of approximately 1620.
2.48 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.
20 0.097 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.
0.048 g of bis(methoxymethylethyl)maleate.

EXAMPLE 20

25 Part A

6.73 g of Part A of Comparative Example 1.

30 Part B

6.73 g of Part B of Comparative Example 1.
0.75 g of FMQ2-type resin having a molecular weight of approximately 1620.
0.78 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.
35 0.002 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.
0.001 g of bis(methoxymethylethyl)maleate.

40 EXAMPLE 21

Part A

20.76 g of Part A of Comparative Example 1.

45 Part B

20.76 g of Part B of Comparative Example 1.
4.55 g of FMQ2.
50 2.02 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.
0.106 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.
0.062 g of bis(methoxymethylethyl)maleate.

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EXAMPLE 22

Part A

5 19.31 g of Part A of Comparative Example 1.

Part B

19.31 g of Part B of Comparative Example 1.

10 4.74 g of a FMQ2-type resin having a molecular weight of approximately 1620.

4.91 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

0.193 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

15 0.096 g of bis(methoxymethylethyl)maleate.

EXAMPLE 23

Part A

20 16.72 g of Part A of Comparative Example 1.

Part B

25 16.72 g of Part B of Comparative Example 1.

6.28 g of FMQ2.

2.8 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

30 0.146 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.085 g of bis(methoxymethylethyl)maleate.

EXAMPLE 24

Part A

35 14.65 g of Part A of Comparative Example 1.

Part B

40 14.65 g of Part B of Comparative Example 1.

8.58 g of FMQ2.

3.82 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

45 0.199 g of a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.116 g of bis(methoxymethylethyl)maleate.

EXAMPLE 25

Part A

50 12.49 g of Part A of Comparative Example 1.

Part B

55 12.49 g of Part B of Comparative Example 1.

10.87 g of FMQ2.

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4.84 g of trimethylsiloxy-terminated methylperfluorobutylethylsiloxane-methylhydrogensiloxane copolymer having approximately 2.3 methylhydrogensiloxane units per methylperfluorobutylethylsiloxane units.

0.252 g of a chloroplatinic acid complex of divinyltetramethylsiloxane diluted with dimethylvinylsiloxy endblocked polydimethylsiloxane to provide 0.7 weight percent platinum.

0.147 g of bis(methoxymethyl)maleate.

Table 1
Swell and Weep Properties of Silicone Elastomers Prepared From Compositions
Containing MQ Resins V. Silicone Elastomers Prepared From Compositions Without Such Resins.

	Comp. Ex. 1	Comp. Ex. 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Wt% Resin	-	-	3.41	6.5	6.5	6.5	6.5	6.5	6.03	8.27	8.41	7.88	7.73	9.5
# vinylsiloxy in molecule	-	-	4	4	4	4	4	4	2	2.5	3	4	6	4
Resin Molecular Weight	-	-	1497	1497	1497	1497	1497	1497	1382	1794	>>950	>>950	1497	
cure time (minutes)	1440	12	1440	960	12	960	12	12	12	12	12	12	12	12
Swell Time (hours)	48	51	48	60	48	48	56	51	51	51	51	51	51	48
% swell at 150 C	27.7	29.2	24.4	20.4	18.3	18.8	18.1	22.9	23.8	23.3	23.6	24.4	21.7	16.9
Weep Time (hours)	24	39	48	48	48	48	48	72	72	72	39	39	39	48
% swell at ambient temp.	20.2	18.1	21.9	18.9	13.4	14	13.2	19.1	20.1	18.9	19.4	21.5	19.5	11.2
Weep #	7.6	11.1	2.4	1.5	4.9	4.8	5	3.8	3.7	4	4.2	2.8	2.2	5.7

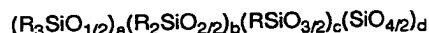
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Table 2
Swell and Weep Properties of Silicone Elastomers Prepared From Compositions Containing Fluorinated-MQ Resins V.
Silicone Elastomers Prepared From Compositions Without Such Resins.

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24	Ex. 25
Wt% Resin	-	-	5.32	10.66	16.03	21.46	26.77	4.38	4.91	5.00	8.77	9.83	13.18	17.81	21.92
# vinyls/resin	-	-	-	4	4	4	4	4	4	4	4	4	4	4	4
Type	Fluorinated	Resin	-	-	-	-	-	-	-	-	-	-	-	-	-
Resin	FMQ1	FMQ1	FMQ1	FMQ1	FMQ1	FMQ1	FMQ1	FMQ2							
Molecular Weight	-	-	>1650	>1650	>1650	>1650	>1650	>5000	1620	1620	>5000	1620	>5000	>5000	>5000
Cure Time (minutes)	1440	12	1440	1440	1440	1440	1440	1440	960	12	1440	960	1440	1440	1440
Swell Time (hours)	48	51	48	48	48	48	48	48	48	56	48	48	48	48	48
% swell at 150 C	27.7	29.2	23.8	20.9	18	19.3	14.4	23.7	23.3	24.3	21.4	21.3	19.1	16.6	14.4
Weep Time (hours)	24	39	24	24	24	24	24	24	48	48	24	48	24	24	24
% swell at ambient	20.2	18.1	21.5	18.1	15.6	15.3	11.7	19.3	21.4	20.4	17.1	19.3	15.6	14.7	11.5
Weep #	7.6	11.1	2.3	2.8	2.4	4	2.7	3.8	2	4	4.3	2	3.5	1.9	2.9

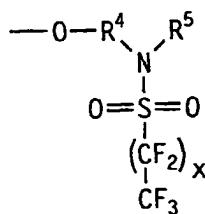
Claims

1. An organosiloxane composition curable to a silicone elastomer, the composition comprising:
 - 5 (A) an alkenyl-containing polydiorganosiloxane having an average of at least two silicon-bonded alkenyl groups per molecule;
 - (B) an organohydrogensiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule, the amount of organohydrogensiloxane present being sufficient to provide a ratio of silicon-bonded hydrogen atoms in component (B) to silicon-bonded alkenyl groups in component (A) of 0.8:1 to 3:1;
 - 10 (C) a platinum group catalyst sufficient for curing the organosiloxane composition; and
 - (D) a resinous organosiloxane copolymer having an average of at least two alkenyl groups per molecule, a number average molecular weight (Mn) between 400 and 15,000 g/mole having the empirical formula:



15 wherein $a > 0$, $d > 0$, $b \geq 0$, $c \geq 0$, $a + b + c + d = 1$, $0 \leq (b + c) \leq 0.2$ and R is a monovalent radical independently selected from hydrogen, hydroxyl, alkyl, alkenyl, alkoxy, -OZ and Z; wherein Z is a fluorine atom-containing group; wherein the sum of the average number of silicon-bonded alkenyl groups per molecule in component (A) and the average number of silicon-bonded hydrogen atoms per molecule in component (B) is greater than four.

- 20 2. The organosiloxane composition of claim 1 wherein at least one of the silicon-bonded organic groups of component (B) is selected from perfluorobutylethyl and 3,3,3-trifluoropropyl.
- 25 3. The organosiloxane composition of any of the preceding claims wherein component (D) has an average of at least two alkenyl groups per molecule.
4. The organosiloxane composition of any of the preceding claims wherein component (D) has at least one fluorine atom-containing group per molecule.
- 30 5. The organosiloxane composition of claim 4 wherein at least an average of one R per molecule of component (D) is an -OZ radical.
6. The organosiloxane composition of claim 5 wherein the -OZ radical is selected from the general formula:



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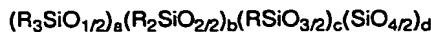
and the general formula:



50 wherein R^4 is an alkylene group having 2 to 6 carbon atoms and $0 \leq x \leq 12$ and R^5 is an alkyl group having 1 to 6 carbon atoms.

- 55 7. The organosiloxane composition of any of the preceding claims wherein component (B) is present in an amount of 5 to 100 parts by weight, per 100 parts by weight of component (A), and component (D) is present in an amount of 1 to 10 parts by weight per 100 parts by weight of component (A).
8. A resinous organosiloxane copolymer having at least one fluorine atom-containing group per molecule, an average

of at least two alkenyl groups per molecule, a number average molecular weight (Mn) between 400 and 15,000 g/mole and having the empirical formula:



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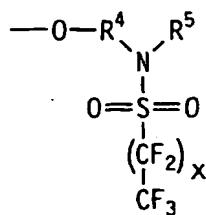
wherein $a > 0$, $d > 0$, $b \geq 0$, $c \geq 0$, $a + b + c + d = 1$, $0 \leq (b + c) \leq 0.2$, and R is a monovalent radical independently selected from hydrogen, hydroxyl, alkyl, alkenyl, alkoxy, -OZ and Z; wherein Z is a fluorine atom-containing group.

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9. The resinous organosiloxane copolymer of claim 8 wherein at least an average of one R per molecule is an -OZ radical.

10. The resinous organosiloxane copolymer of claim 9 wherein the -OZ radical is selected from the general formula:

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and the general formula:



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wherein R^4 is an alkylene group having 2 to 6 carbon atoms and $0 \leq x \leq 12$ and R^5 is an alkyl group having 1 to 6 carbon atoms.

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11. A silicone elastomer obtainable by

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- (I) preparing the organosiloxane composition of any of claims 1-7; and
- (II) allowing the organosiloxane composition to cure.

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12. A method of minimizing the leakage of hydrocarbon fluid from a container, the method comprising the steps of

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- (I) preparing the organosiloxane composition of any of claims 1-7;
- (II) applying the organosiloxane composition to a surface on the container; and
- (III) allowing the composition to cure.

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13. A method of minimizing the leakage of hydrocarbon fluid from a container, the method comprising the steps of

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- (I) preparing the organosiloxane composition of any of claims 1-7;
- (II) allowing the composition to cure to a silicone elastomer; and
- (III) sealing the container by securing the cured elastomer to a surface on the container.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 97122478.7						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim		CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)					
D, A	<u>US 5292586 A</u> (LIN et al.) 08 March 1994 (08.03.94), claims. --	1-11	C 08 L 83/04 C 08 L 83/08 C 09 K 3/10						
A	<u>EP 0337790 A2</u> (DOW CORNING CORPORATION) 18 October 1989 (18.10.89), claims. --	1-11							
D, A	<u>US 5574073 A</u> (JUEN et al.) 12 November 1996 (12.11.96), claim 2. --	1-11							
A	<u>EP 0573282 A1</u> (SHIN-ETSU CHEMICAL CO, LTD.) 08 December 1993 (08.12.93), page 2, lines 10-14, page 6, lines 30,31, claims. ----	1							
			TECHNICAL FIELDS SEARCHED (Int. Cl. 6)						
			C 08 L C 09 K C 09 J						
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search VIENNA</td> <td>Date of completion of the search 08-04-1998</td> <td>Examiner TENGLER</td> </tr> <tr> <td colspan="3"> CATEGORY OF CITED DOCUMENTS <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> </td> </tr> </table>				Place of search VIENNA	Date of completion of the search 08-04-1998	Examiner TENGLER	CATEGORY OF CITED DOCUMENTS <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>		
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